

## CLAIMS

*What is claimed is:*

1. A system for cleaning semiconductor wafers, the system comprising:
  - a solvent delivery mechanism configured to provide a supercritical cleaning solution;
  - a process vessel in downstream fluid communication with the solvent delivery mechanism, said process vessel comprising a wafer support; and
  - a recirculation system in fluid communication with the process vessel, said recirculation system configured to allow the supercritical cleaning solution to recirculate through the process vessel such that a flow field is established over at least one surface of a wafer or a plurality of wafers in the wafer support to thereby clean the surface or surfaces that contact the flow field.
2. The system of claim 1, wherein the solvent delivery mechanism comprises:
  - a source of a sub-critical cleaning solvent or a sub-critical cleaning solution in a liquid state;
  - an inlet configured to receive the sub-critical cleaning solvent or the sub-critical cleaning solution and deliver it to;
  - a supercritical solution generator configured to convert the sub-critical cleaning solvent or the sub-critical cleaning solution into the supercritical cleaning solution; and
  - an outlet configured to deliver the supercritical cleaning solution from the supercritical solution generator to the process vessel.
3. The system of claim 2, further comprising an additive delivery mechanism, said additive delivery mechanism configured to provide a chemical additive to at least one of the

sub-critical cleaning solvent, the sub-critical cleaning solution, or the supercritical cleaning solution.

4. The system of claim 2, wherein the supercritical solution generator comprises:
  - a pump configured to pressurize the sub-critical cleaning solvent or the sub-critical cleaning solution to at least its critical point; and
  - a heat exchanger in fluid communication with the pump, said heat exchanger configured to heat the sub-critical cleaning solvent or the sub-critical cleaning solution to at least its critical temperature.
5. The system of claim 4, further comprising:
  - a pressure sensor configured to measure the pressure in the process vessel; and
  - a pressure controller configured to control the pressure in the process vessel in response to pressure information from the pressure sensor;wherein control is achieved by adjustment of at least one of the pump and the heat exchanger.
6. The system of claim 4, wherein the solvent delivery mechanism further comprises a buffer vessel in downstream fluid communication with the heat exchanger, said buffer vessel capable of storing between about 5 and 25 times the volume of the supercritical cleaning solution than the combined volume of the process vessel and the recirculation system.
7. The system of claim 6, further comprising:
  - a first pressure sensor configured to measure the pressure in the process vessel;
  - a flow control valve in downstream fluid communication with the buffer vessel; and
  - a first pressure controller configured to control the pressure in the process vessel in response to pressure information from the first pressure sensor;

wherein control is achieved by adjustment of the flow control valve.

8. The system of claim 7, further comprising:

a second pressure sensor configured to measure the pressure in the buffer vessel;  
and

a second pressure controller configured to control the pressure in the buffer vessel in response to pressure information from the second pressure sensor;

wherein control is achieved by adjustment of at least one of the pump and the heat exchanger.

9. The system of claim 3, wherein the recirculation system comprises the additive delivery mechanism, said additive delivery mechanism configured to provide the chemical additive to the supercritical cleaning solution.

10. The system of claim 1, wherein the recirculation system comprises:

a pump configured to move the supercritical cleaning solution through the recirculation system;

an inline static mixer configured to provide a circuitous path to the supercritical cleaning solution.

11. The system of claim 10, wherein the recirculation system further comprises:

a first particulate filter in upstream fluid communication with the pump, said first particulate filter configured to remove particulates from the supercritical cleaning solution before said supercritical cleaning solution enters the pump; and

a second particulate filter in upstream fluid communication with the process vessel, said filter configured to remove particulates from the supercritical cleaning solution before said supercritical cleaning solution enters the process vessel.

12. The system of claim 11, wherein the recirculation system further comprises a differential pressure transducer configured to measure the pressure in the recirculation system at a point upstream from the first particulate filter and at a point downstream from the second particulate filter.

13. The system of claim 12, wherein pressure information from the differential pressure transducer is used to control flow of the supercritical cleaning solution through the recirculation system.

14. The system of claim 1, wherein the recirculation system comprises isolation valves for stopping fluid communication of the recirculation system with the process vessel.

15. The system of claim 1, further comprising a depressurization system configured to vent the supercritical cleaning solution from the system.

16. The system of claim 15, wherein the depressurization system is configured to vent the supercritical cleaning solution from the process vessel.

17. The system of claim 15, wherein the depressurization system comprises a plurality of control valves in parallel fluid communication, said plurality of control valves comprising:

- a first exhaust flow control valve configured to meter the release of the supercritical cleaning solution no faster than said supercritical cleaning solution can be introduced into the process vessel by the solvent delivery mechanism;

- a second exhaust control valve having a higher flow coefficient than the first exhaust control valve; and

- a dump valve having a higher flow coefficient than the second exhaust control valve.

18. The system of claim 15, further comprising a solvent recycle system in downstream fluid communication with the depressurization system, said solvent recycle system configured to capture vapor resulting from release of the supercritical cleaning solution by the depressurization system.

19. The system of claim 18, wherein the sub-critical media is purified after capture to produce a recycled solvent.

20. The system of claim 19, wherein the recycled solvent is delivered to the solvent delivery mechanism for use in production of the supercritical cleaning solution.

21. The system of claim 19, wherein the sub-critical media is purified by a method comprising at least one of filtration, distillation, liquid-gas phase-separation, and use of semi-permeable membranes.

22. The system of claim 1, wherein the process vessel comprises a first and a second plate, which when mated create a process cavity that encloses the wafer support.

23. The system of claim 22, wherein the process vessel comprises a corrosion resistant material.

24. The system of claim 23, wherein the corrosion resistant material comprises at least one of stainless steel, aluminum, titanium, hastelloy, and a nickel-iron alloy.

25. The system of claim 22, wherein the process cavity has a plurality of plenums configured to receive the supercritical cleaning solution from a process vessel inlet.

26. The system of claim 22, wherein the process vessel further comprises:
- a slot configured to allow insertion of the wafer or the plurality of wafers into the process vessel; and
  - a door mechanism configured to seal the slot while the process vessel is charged with the supercritical solution.
27. The system of claim 26, wherein the door mechanism comprises a sealing mechanism configured to allow internal pressure in the process vessel to reinforce its sealing ability.
28. The system of claim 22, further comprising:
- a primary seal configured to form a fluid-tight seal between the first and second plates when mated; and
  - a secondary seal configured to form a fluid-tight seal between the first and second plates when mated.
29. The system of claim 28, wherein the primary seal is a self-energized bore seal.
30. The system of claim 28, wherein the primary seal is a spring-energized U-cup seal.
31. The system of claim 28, wherein the secondary seal comprises two or more distinct sealing members.
32. The system of claim 28, wherein the secondary seal comprises at least one of a metal gasket, an elastomeric O-ring, a spring-energized U-cup, a T-seal, and a back-up seal.

33. The system of claim 28, wherein the primary and secondary seals comprise at least one of Viton, EPDM, silicone, Kalrez, Chemrez, polyurethane, fluoropolymer, aluminum, brass, copper, stainless steel, and nickel.

34. The system of claim 32, wherein the back-up seal comprises at least one of fiberglass-reinforced plastic, polyvinyl chloride, pvdf-Kynar, Delrin.

35. The system of claim 25, further comprising a plurality of flow distribution manifolds each dimensioned to mate with one of the plurality of plenums, when mated, said plurality of plenums and flow distribution manifolds are configured to create the flow field.

36. The system of claim 35, wherein each of the plurality of flow distribution manifolds comprises a plurality of holes configured to direct flow of the supercritical cleaning solution from its corresponding plenum to the process cavity.

37. The system of claim 35, wherein each of the plurality of flow distribution manifolds comprises a plurality of grooves configured to direct the flow of the supercritical cleaning solution from its corresponding plenum and onto an interior surface of the process cavity before flowing onto said at least one surface of the wafer or plurality of wafers.

38. The system of claim 37, wherein each of the plurality of grooves comprises between about 8 and 72 grooves.

39. The system of claim 38, wherein the angular interval between grooves is between about 5 and 45 degrees.

40. The system of claim 39, wherein the angle of tangency is between about 15 and 75 degrees.

41. The system of claim 35, wherein the plurality of flow distribution manifolds comprise at least one of stainless steel, hastalloy, aluminum, titanium, and nickel-iron alloys.

42. The system of claim 1, wherein the wafer support comprises:

a plurality of point contacts configured to support the wafer or plurality of wafers while making minimal contact with the wafer or plurality of wafers; and

a plurality of wafer guides configured to position the wafer or plurality of wafers in the wafer support.

43. The system of claim 42, wherein the plurality of point contacts and wafer guides comprises at least one of quartz, ruby, sapphire, ceramic alumina, aluminum, and titanium.

44. The system of claim 1, wherein the wafer support comprises a wafer rotation mechanism, the wafer rotation mechanism configured to allow rotation of the wafer or plurality of wafers during processing.

45. The system of claim 44, wherein the wafer rotation mechanism comprises a magnetically coupled drive.

46. The system of claim 1, wherein the system is configured to such that the flow field produces approximately equal fluid pressure and flow dynamics on both sides of the wafer or plurality of wafers.

47. The system of claim 1, wherein the process vessel comprises a heater configured to heat one or more walls of the process vessel.

48. The system of claim 1, wherein the recirculation system comprises a heater configured to maintain the temperature of the supercritical cleaning solution as it traverses the recirculation system.



49. The system of claim 3, wherein the process vessel comprises the additive delivery mechanism, said additive delivery mechanism configured to provide the chemical additive to the supercritical cleaning solution.

50. The system of claim 3, wherein the solvent delivery mechanism comprises the additive delivery mechanism, said additive delivery mechanism configured to provide the chemical additive to the supercritical cleaning solution.

51. The system of claim 3, wherein the recirculation system comprises the additive delivery mechanism, said additive delivery mechanism configured to provide the chemical additive to a solvent to produce the sub-critical cleaning solution.

52. The system of claim 3, wherein the additive delivery mechanism comprises a syringe pump configured to deliver a liquid to the supercritical cleaning solution without the supercritical cleaning solution losing its supercritical state.

53. The system of claim 6, wherein the buffer vessel comprises a heater configured to maintain the temperature of the supercritical cleaning solution in the buffer vessel.

54. The system of claim 1, further comprising a pulsing mechanism coupled to at least one of the recirculation system and the process vessel, said pulsing mechanism configured to control the pressure of the supercritical cleaning solution to which the wafer or plurality of wafers are exposed in manner that provides a pulsed pressure distribution.

55. The system of claim 35, wherein the of plurality of flow distribution manifolds further comprises a plurality of contoured surfaces configured to mediate the flow field.

56. The system of claim 55, wherein the plurality of contoured surfaces comprises at least one of fins, chevrons, baffles, convexities, and concavities.

57. The system of claim 42, wherein each of the plurality of wafer guides are inclined at an angle of between about 60 and 85 degrees to the vertical (perpendicular to the wafer support surface) and are arranged around the periphery of the wafer or each of the plurality of wafers.

58. The system of claim 11, wherein the first and second particulate filters are self-cleaning filters.

59. The system of claim 35, wherein at least one of the plurality of flow distribution manifolds is a showerhead.

60. A system for cleaning semiconductor wafers, the system comprising:

a solvent delivery mechanism configured to provide a cleaning solvent, a cleaning solution, or a supercritical cleaning solution comprising the cleaning solvent or the cleaning solution, said solvent delivery mechanism comprising:

(i) an inlet configured to receive the cleaning solvent or the cleaning solution in a sub-critical liquid state;

(ii) a pressure mechanism configured to pressurize the cleaning solvent or the cleaning solution to at least about the critical pressure of the cleaning solvent or the cleaning solution; and

(iii) a heating mechanism configured to heat the cleaning solvent or the cleaning solution to at least about their critical temperature; and

a process vessel in fluid communication with the solvent delivery mechanism and comprising a wafer support, and configured to support the supercritical cleaning solution.

61. The system of claim 60, wherein the solvent delivery mechanism further comprises a buffer vessel configured to store between about 5 and 25 times the volume of the process vessel, said buffer vessel configured to directly supply the cleaning solvent, the cleaning solution, or the supercritical cleaning solution to the process vessel.

62. The system of claim 60, further comprising a recirculation system configured to recirculate the cleaning solvent, the cleaning solution, or the supercritical cleaning solution through the process vessel.

63. The system of claim 62, further comprising a valve configured to allow delivery of the cleaning solvent, cleaning solution, or supercritical cleaning solution from the solvent delivery mechanism to the process vessel, wherein the valve is controllable to be shut off or partially shut off while the recirculation system recirculates the cleaning solvent, cleaning solution, or supercritical cleaning solution through the process vessel.

64. The system of claim 60, further comprising a heater for heating one or more walls of the process vessel.

65. The system of claim 60, wherein the wafer support is configured to a wafer or a plurality hold a plurality of wafers.

66. The system of claim 65, wherein the process vessel is configured to allow the cleaning solvent, the cleaning solution, or the supercritical cleaning solution to contact both the front side and back side of the wafer or each of the plurality of wafers to thereby allow cleaning thereon.

67. The system of claim 60, wherein the process vessel comprises a chemical additive delivery mechanism for providing chemical additives to the cleaning solvent, the cleaning solution, or the supercritical cleaning solution.

68. The system of claim 62, wherein the recirculation system comprises a chemical additive delivery mechanism for providing chemical additives to the cleaning solvent, the cleaning solution, or the supercritical cleaning solution.

69. The system of claim 60, wherein the solvent delivery system further comprises a chemical additive delivery mechanism for providing chemical additives to the cleaning solvent, the cleaning solution, or the supercritical cleaning solution.

70. A system for cleaning semiconductor wafers, the system comprising:

- a process vessel arranged to receive a cleaning solvent, a cleaning solution, or a supercritical cleaning solution comprising the cleaning solvent or the cleaning solution, said process vessel comprising a wafer support and being constructed to support the supercritical cleaning solution;
- a recirculation system in fluid communication with the process vessel in a manner allowing the cleaning solvent, the cleaning solution, or the supercritical cleaning solution to recirculate through the process vessel and causing a flow field to be established over at least one surface of a wafer or at least one surface of each wafer of a plurality of wafers to thereby clean said at least one surface; and
- a mixing region in the recirculation system, said mixing region comprising a mechanism designed to mix chemical additives with the cleaning solvent, the cleaning solution, or the supercritical cleaning solution.

71. The system of claim 70, further comprising a solvent delivery mechanism configured to provide the cleaning solvent, the cleaning solution, or the supercritical solution to the process vessel, said solvent delivery mechanism comprising:

- (i) an inlet configured to receive the cleaning solvent or the cleaning solution in a sub-critical liquid state;

- (ii) a pressure mechanism configured to pressurize the cleaning solvent or the cleaning solution to at least about the critical pressure of the cleaning solvent or the cleaning solution;
- (iii) a heating mechanism configured to heat the cleaning solvent or the cleaning solution to at least about their critical temperature.

72. The system of claim 71, wherein the solvent delivery mechanism further comprises a buffer vessel configured to store between about 5 and 25 times the volume of the process vessel, said buffer vessel configured to supply the cleaning solvent, the cleaning solution, or the supercritical cleaning solution to the process vessel.

73. The system of claim 71, further comprising a valve configured to allow delivery of the cleaning solvent, cleaning solution, or supercritical cleaning solution from the solvent delivery mechanism to the process vessel, wherein the valve is controllable to be shut off or partially shut off while the recirculation system recirculates the cleaning solvent, cleaning solution, or supercritical cleaning solution through the process vessel.

74. The system of claim 70, further comprising a heater for heating one or more walls of the process vessel.

75. The system of claim 70, wherein the process vessel comprises a chemical additive delivery mechanism for providing chemical additives to the cleaning solvent, the cleaning solution, or the supercritical cleaning solution.

76. The system of claim 70, wherein the recirculation system comprises a chemical additive delivery mechanism for providing chemical additives to the cleaning solvent, the cleaning solution, or the supercritical cleaning solution.

77. The system of claim 71, wherein the solvent delivery system further comprises a chemical additive delivery mechanism for providing chemical additives to the cleaning solvent, the cleaning solution, or the supercritical cleaning solution.

78. A system for cleaning semiconductor wafers, the system comprising:

a process vessel comprising a wafer support and constructed to support a supercritical cleaning solution comprising a cleaning solvent or cleaning solution;

a recirculation system in fluid communication with the process vessel in a manner allowing the cleaning solvent, the cleaning solution, or the supercritical cleaning solution to recirculate through the process vessel and causing a flow field to be established over at least one surface of a wafer, to thereby clean the wafer; and

a dilution system coupled to the process vessel and comprising:

a first valve configured to allow introduction of the supercritical cleaning solution into the process vessel; and

a second valve arranged to at least partially release the supercritical cleaning solution from the process vessel,

wherein dilution of the supercritical cleaning fluid is performed without loss of supercritical conditions within the process vessel.

79. The system of claim 78, further comprising a solvent delivery mechanism configured to provide the cleaning solvent, the cleaning solution, or the supercritical solution to the process vessel, said solvent delivery mechanism comprising:

(i) an inlet configured to receive the cleaning solvent or the cleaning solution in a sub-critical liquid state;

(ii) a pressure mechanism configured to pressurize the cleaning solvent or the cleaning solution to at least about the critical pressure of the cleaning solvent or the cleaning solution;

- (iii) a heating mechanism configured to heat the cleaning solvent or the cleaning solution to at least about their critical temperature.

80. The system of claim 79, wherein the solvent delivery mechanism further comprises a buffer vessel configured to store between about 5 and 25 times the volume of the process vessel, said buffer vessel configured to directly supply the cleaning solvent, the cleaning solution, or the supercritical cleaning solution to the process vessel.

81. The system of claim 79, further comprising a valve configured to allow delivery of the cleaning solvent, cleaning solution, or supercritical cleaning solution from the solvent delivery mechanism to the process vessel, wherein the valve is controllable to be shut off or partially shut off while the recirculation system recirculates the cleaning solvent, cleaning solution, or supercritical cleaning solution through the process vessel.

82. The system of claim 78, further comprising a heater for heating one or more walls of the process vessel.

83. The system of claim 78, wherein the process vessel comprises a chemical additive delivery mechanism for providing chemical additives to the cleaning solvent, the cleaning solution, or the supercritical cleaning solution.

84. The system of claim 78, wherein the recirculation system comprises a chemical additive delivery mechanism for providing chemical additives to the cleaning solvent, the cleaning solution, or the supercritical cleaning solution.

85. The system of claim 79, wherein the solvent delivery system further comprises a chemical additive delivery mechanism for providing chemical additives to the cleaning solvent, the cleaning solution, or the supercritical cleaning solution.

86. A method of cleaning a semiconductor wafer, the method comprising:
- providing the wafer to a process vessel;
  - preparing a supercritical cleaning solution;
  - providing the supercritical cleaning solution to the process vessel; and
  - recirculating the supercritical cleaning solution through the process vessel in a manner causing a flow field to be established over at least one surface of the wafer, to thereby clean the wafer.
87. The method of claim 86, wherein the flow field is established over the front and back side surfaces of the wafer to clean both the front and back side surfaces of the wafer.
88. The method of claim 86, wherein the materials to be removed from the wafer comprise at least one of photoresist, post-etch residue, moisture, metals, inorganic materials, and organic contaminants.
89. The method of claim 86, wherein providing the wafer to the process vessel comprises positioning the wafer on a support in the process vessel in a manner that presents open access to both the front side and back side surfaces of the wafer.
90. The method of claim 86, wherein preparing the supercritical cleaning solution comprises:
- (i) providing a sub-critical solvent or a sub-critical cleaning solution;
  - (ii) raising the pressure of the sub-critical solvent or the sub-critical cleaning solution to at least its critical pressure; and
  - (iii) raising the temperature of the sub-critical solvent or the sub-critical cleaning solution to at least its critical temperature.
91. The method of claim 90, wherein (ii) is performed before (iii).
92. The method of claim 91, wherein the sub-critical solvent or the sub-critical cleaning solution comprises carbon dioxide.



93. The method of claim 90, wherein preparing the supercritical cleaning solution comprises:

converting the sub-critical solvent into a supercritical solvent; and  
introducing one or more additives into the supercritical solvent.

94. The method of claim 93, wherein the one or more additives are selected from the group consisting of reagents that chemically or physically react with a material to be cleaned from the wafer, a chelating agent that chelates one or more metal ions in the material to be cleaned from the wafer, a surfactant that assists in cleaning the material from the wafer, an anti-corrosion agent that protects a material on the surface of the wafer, a co-solvent that increases the solubility of any one or more of the foregoing in the supercritical solvent, and combinations thereof.

95. The method of claim 93, wherein the one or more additives are added in a line feeding the process vessel.

96. The method of claim 93, wherein the one or more additives are added to the process vessel.

97. The method of claim 93, wherein the one or more additives are added in a recirculation loop through which the supercritical cleaning solution recirculates.

98. The method of claim 93, further comprising mixing the one or more additives with the supercritical solvent by passing the supercritical solvent and said one or more additives through a flow element that produces turbulent flow.

99. The method of claim 86, wherein the supercritical cleaning solution comprises supercritical carbon dioxide and one or more additives that facilitate cleaning of the wafer.

100. The method of claim 86, wherein recirculating the supercritical cleaning solution comprises recirculating in a closed loop.

101. The method of claim 86, further comprising introducing a supercritical solvent to the process vessel to remove the supercritical cleaning solution after the wafer has been cleaned.

102. The method of claim 101, wherein introducing a supercritical solvent to the process vessel to remove the supercritical cleaning solution after the wafer has been cleaned comprises:

opening an inlet valve to allow introduction the supercritical solvent into the process vessel; and

opening a first outlet valve to vent the supercritical cleaning solution from the process vessel and simultaneously introduce the supercritical solvent into the process vessel;

wherein the rate of introduction of the supercritical solvent and the rate of venting of the supercritical cleaning solution are adjusted so that supercritical conditions are maintained in the process vessel.

103. The method of claim 102, further comprising opening a second outlet valve to at least partially depressurize the process vessel and render the supercritical solvent sub-critical.

104. The method of claim 103, further comprising:

opening a third outlet valve, after the second outlet valve was opened, to complete depressurizing the process vessel; and

removing the wafer from the process vessel.

105. The method of claim 86, wherein providing the supercritical cleaning solution to the process vessel comprises:

generating the supercritical cleaning solution; and

storing the supercritical cleaning solution in a buffer vessel before providing the supercritical cleaning solution to the process vessel, said buffer vessel configured to store between about 5 and 25 times the volume of the supercritical cleaning solution than the volume of the process vessel.

106. The method of claim 86, further comprising sensing a pressure differential between inlet and outlet lines of a recirculation loop to determine whether the supercritical cleaning solution is flowing properly.

107. The method of claim 86, further comprising pulsing the pressure of the supercritical cleaning solution recirculating through the process vessel while cleaning the wafer.

108. The method of claim 102, further comprising:

capturing the effluent from venting the supercritical cleaning solution with a recapture-recycle system; and

purifying any solvents that the effluent contains with the recapture-recycle system.

109. The method of claim 108, wherein purifying said any solvents that the effluent contains comprises at least one of filtration, distillation, liquid-gas phase-separation, and using semi-permeable membranes.

110. The method of claim 108, wherein the effluent is captured at between about 100 and 500 psi.

111. The method of claim 107, wherein pulsing the pressure of the supercritical cleaning solution recirculating through the process vessel is performed at between about 1 and 10 cycles per minute.